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t: MAGNETIC PROPERTIES OF SOME MACROMOLECULES OF BIOLOGICAL INTEREST

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Introduction

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This report outlines progress during the first three months of a basic research study. The aims of this research are to measure the magnetic susceptibility of some selected macromolecules over a wide range of temperature and magnetic fields, and to attempt to correlate the results of these measurements with the structure and with the physical and chemical properties of the compounds. Of particular interest is the possibility of detecting effects due to the quantized collective motion of electrons in large molecules. In large molecules in high magnetic fields, there may be observable changes in the diamagnetic susceptibility which may be related to the multiple connectivity of the molecules, and these changes may give information about molecular structure.

A primary incentive for these measurements is the recent appearance of extremely sensitive new techniques for measuring magnetic flux. These techniques are being developed at Stanford University in conjunction with experiments on quantized magnetic flux in superconductors. These techniques, together with superconducting magnetic shields and superconducting persistent current magnets, make possible entirely new kinds of magnetic measurements.

A concurrent aim of this research is to adapt these new techniques, which have sensitivity and magnetic field range potentialities much greater than existing methods, to the measurement of magnetic susceptibility.

Work during this first period was devoted to design and construction of equipment and to procurement of the complex organic compounds to be studied. A brief description of the apparatus and chemicals follows.

Susceptibility Apparatus. The principal component of the susceptibility apparatus to be used in this project is the modulated inductance detector which is diagrammed in Fig. 1. The total magnetic flux encircled by the closed superconducting loop or circuit is constant, because the electrical resistance is zero. If an external field is applied which would cause a flux change through the loop, the loop reacts by inducing a current which produces an exactly equal and opposite flux change. Thus the total flux through the loop remains constant. The superconducting induced current will persist forever or until the flux change has been removed. A normal conducting circuit will also oppose a flux change through it by an induced current, but the current will decay to zero because of the electrical resistance. The persistent current in the superconducting circuit is a permanent record of the flux change which was attempted on the circuit. If this current can be measured, it will be proportional to the attempted change.

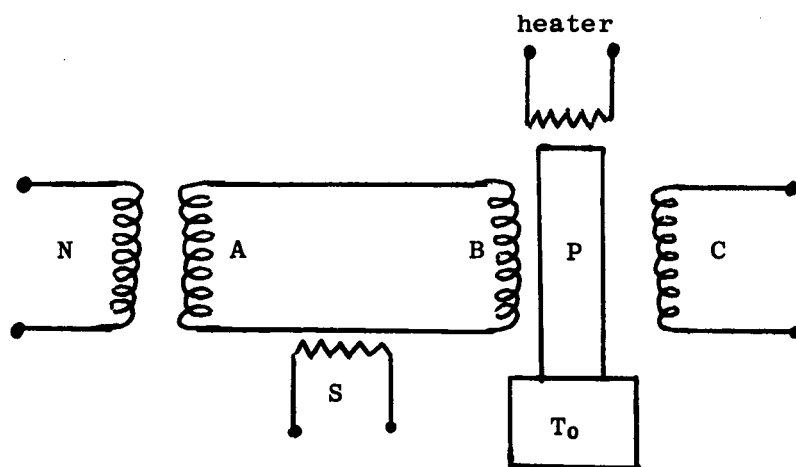


Figure 1

The operation of the circuit to measure a magnetic flux change is as follows. First, any persistent current already present in the circuit A-B is eliminated by momentarily heating a small region of the circuit with switch heater S, causing a normal resistance in that part of the circuit and thus causing any currents to decay to zero. If the coil is returned to the superconducting state and a magnetic flux change is caused in coil A, a current will be induced in circuit A-B which produces flux in A and flux in B whose sum is exactly equal and opposite to the attempted flux change in A, thus maintaining the flux through the circuit A-B at its initial zero value. To measure the persistent current, coil B and a secondary coil C are wound around a superconducting post P. The superconducting post P is thoroughly grounded at one end to a temperature T_0 below its superconducting transition temperature. The other end can be periodically heated so that the post rises above its superconducting transition temperature and then cools back to the superconducting state. When the post is normal the current flowing in B causes a magnetic flux to link both B and C. When the post goes superconducting, the magnetic flux inside the post is expelled because of the Meissner effect, thus changing the amount of flux linking B and C. As the post is heated and cooled periodically, the periodic variation of the flux in C causes an alternating voltage across the coil C. This voltage can be measured and is proportional to the persistent current flowing in circuit A-B, and consequently proportional to the attempted flux change in coil A.

The circuit is readily adaptable to the measurement of magnetic susceptibility. A sample whose susceptibility is to be determined is inserted into coil A and an external magnetic field is applied to A and the sample. The switch S is turned on momentarily to eliminate persistent currents in the circuit A-B, and the circuit is allowed to return to the superconducting state. Then the sample is removed from coil A, causing a flux change in A which is proportional to the magnetization of the sample and consequently proportional to its susceptibility. The signal from C is thus also proportional to the susceptibility.

A somewhat improved measurement may be possible by providing an additional coil N concentric with pickup coil A. A current in N will cause the flux through A to change; when the change is exactly equal and opposite to that caused by the removal of the sample, there will be no necessity for a current in the circuit A-B, and consequently the signal from coil C will be zero. At this null condition the current in N is directly proportional to the susceptibility of the sample.

The device may be calibrated either against a sample of the same shape and size with known susceptibility or by calculation from the geometry of coils N and A and the size and position of the sample.

Since variations in the applied field will cause flux changes through A, this field must be extremely stable if small susceptibilities are to be measured without being masked by field variations. Thus the extreme stability afforded by superconducting, persistent-current magnets is necessary. Also fields of tens of kilogauss are readily obtainable with

small and relatively simple superconducting solenoids. Since magnetic field changes in coils A and B from all sources cause variations in the persistent current being measured, these coils must be shielded from all external sources of field and from each other. This shielding is most successfully accomplished with one superconducting container around coil A and a second one around the remainder of the detecting circuit.

Superconducting circuit, magnets, and shields must operate at liquid helium temperatures. However, a variable-temperature sample space can be provided by inserting a small double-walled Dewar vessel inside coil A.

During the last eight months SRI has devoted approximately two man-years at its own expense to the design and construction of an apparatus embodying the principles described above. (In addition the apparatus provides for varying the sample chamber temperature from approximately 1°K up to room temperature.) Because construction had not been completed by 1 November, only 4 percent of the contract funds have been expended. These funds were devoted to additional design and construction of sample holders and sample chamber required specifically for the organic samples to be accommodated by the basic cryostat (which also is being constructed at Institute expense), and to the selection and procurement of sample material. Major construction and assembly should be completed by 1 December, and initial measurements will be made as soon as possible thereafter.

Sample Selection. Three types of compounds have been selected to provide candidates for the initial susceptibility measurements. All contain large conjugated rings and may be capable of giving rise to interesting effects in high magnetic fields. The first is the group of anulenes being synthesized by F. Sondheimer at the Weizmann Institute of Israel;¹ these are large single-ring hydrocarbons containing as many as 30 carbon atoms ($C_{30}H_{30}$ or (30) anulene). The second is the group of condensed-ring molecules, coronene, $C_{24}H_{12}$, ovalene, $C_{32}H_{14}$, and circum-anthracene, $C_{40}H_{16}$, which have been produced by E. Clar at the University of Glasgow.² The third group is porphyrins and phthalocyanines. These are related to hemin and myoglobin which are desirable candidates for measurements in later stages of this program.

¹ Sondheimer, F., R. Wolovsky, and Y. Amiel, J. Am. Chem. Soc. 84, 274 (1962)

² Clar, E., et al., J. Chem. Soc. 3878 (October 1956)

Requests for information and for assistance in obtaining sample material have been sent to Professors Sondheimer and Clar and to seven other laboratories and organic chemical suppliers in this country and in Europe. Samples of the more readily available materials have been purchased from standard suppliers. These will be purified and then examined spectroscopically for impurities before making susceptibility measurements. Initial measurements will be made on polycrystalline materials. However, after the techniques have been developed it is hoped that measurements can be made on single-crystal material along three mutually perpendicular axes, to determine diamagnetic anisotropy. A purified sample of coronene is scheduled to be available for the first experiments with organic compounds about 15 December.